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A CHEMICAL STUDY OF THE LIME AND SULFUR DIP.

By ROSCOE H. SHAW, Manhattan.

LIME and sulfur dips were brought to the writer's attention some two years ago by Dr. N. S. Mayo, at that time state veterinarian. The problem to be solved then was the remedying of a turbidity which ensued when the concentrated ooze was diluted with the ordinary hard water of the Western plains. One thing led to another, until the work extended intermittently over a period of about one year. Among the phases of the subject taken up was one concerning the chemical changes taking place in the dip when exposed in open vats. Such exposure is the usual occurrence in practice when two immersions are made with a ten-day period between them. During this interval the vats are sometimes partly covered with boards, but more often are left entirely exposed.

The purpose of this paper is to present some of the results obtained in this phase of the investigation.

The dip used was made according to the Fort Collins formula, as given in Bulletin No. 21 of the Bureau of Animal Industry, Department of Agriculture. According to this formula, lime and sulfur, in the proportion of one to three, are boiled with water. Commercial lime and ordinary flowers of sulfur were employed and distilled water used in diluting.

In order that laboratory conditions should conform as closely as might be with those obtaining on the ranch, miniature vats were constructed of wood, with all cracks and seams made tight with paraffin. The vat containing the dip which is discussed in this paper was of the style known as the swimming vat, a type in common use in western Kansas. It was eight feet long, six inches deep, and five inches wide.

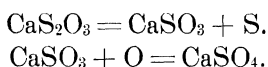
The vat was filled with dip made as before stated, but diluted somewhat more than is called for by the formula. Each morning, at a definite hour, the contents of the vat were mixed and sampled. During the day a crust formed, which was broken up each morning in order to secure something of the effect of the wind on the vats in practical use. Under ordinary conditions the wind also accelerates the evaporation, but in this experiment no attempt was made artificially to produce the result. Another difference was that the vat, being indoors, was not exposed to sudden changes of temperature, such as would occur in practice.

In sampling, small quantities were taken from different parts of the vat; these were well mixed and a subsample taken for analysis. Care was taken to start the determinations immediately after sampling.

The diluted dips are of an orange-red color. On standing exposed to the air an incrustation soon forms, which consists of calcium carbonate and free sulfur. If this incrustation is broken it falls to the bottom of the containing vessel and a fresh incrustation forms. A slight jarring or even a breath of wind is sufficient to break up this crust; so after standing for some time there will be a layer of sediment on the bottom of the vessel as well as a crust on top, both being of the same chemical composition.

Qualitative analysis of the dip showed presence of calcium sulfides, polysulfides, and thiosulfate. At all times hydrogen sulfide was evolved, due probably to the action of the atmospheric carbon dioxide on the sulfide.

If sulfites and sulfates were present they were in such slight amounts as would be negligible. The absence of quantitative amounts of the last two was somewhat surprising, as it is well known that thiosulfates in solution are converted slowly to sulfites and sulfates according to these reactions:



If this decomposition and oxidation takes place in the dip at all it takes place very slowly.

To the writer's knowledge there is no method known for separating the polysulfides of calcium. An attempt was made by employing a freezing mixture of snow and calcium chloride and partially freezing the concentrated ooze, as the dip is called before diluting. The chemical composition of the frozen and the unfrozen portions showed, however, that little or no separation was accomplished.

Necessarily, then, the determinations were limited to those of total sulfur, total calcium, and calcium thiosulfate. By subtracting the calcium and sulfur calculated from the percentage of the thiosulfate from the total calcium and sulfur, percentages were obtained which represented, approximately at least, the calcium and sulfur existing in the combined sulfides. In no case in a large number of analyses of dip did this percentage correspond to that of any one of the polysulfides. Usually it fell between the tetrasulfide and pentasulfide, and could always be assigned to a mixture of the mono- and the pentasulfide. This will be spoken of later in the paper.

The specific gravity was determined in each case, both as a factor in itself and as a means for converting volume into weight.

QUANTITATIVE METHODS EMPLOYED.

Determination of Specific Gravity.—The determinations of specific gravity were made by means of a Geissler's pycnometer, with a capacity of about fifty cubic centimeters, and provided with a delicate thermometer.

Determination of Thiosulfate.—In this determination the sulfides of calcium were removed by means of cadmium. Five cubic centimeters of the dip were stirred into about twenty-five cubic centimeters of freshly boiled distilled water to which had been added a quantity of a five-per-cent. solution of cadmium chloride sufficient to completely precipitate the sulfides. The resulting cadmium sulfide settled at once, was quickly filtered off, and left a clear filtrate. This filtrate was titrated with decinormal iodine solution, using freshly prepared starch as indicator.

Determination of Calcium.—Twenty-five cubic centimeters of the dip were pipetted into a 250 cubic centimeter measuring flask and diluted to the mark with freshly boiled distilled water; twenty-five cubic centimeters, representing two and one-half cubic centimeters of the original dip, were immediately pipetted out into a beaker; two cubic centimeters of a saturated solution of potassium hydroxide and an excess of bromine water added. The beaker with contents was then placed on a hot plate and digested at just below the boiling-point to the complete oxidation of the sulfur. After cooling, hydrochloric acid was added to acid reaction and the excess of bromine removed by reheating. Ammonia was added to alkalinity and the calcium precipitated by adding a sufficient quantity of five-per-cent. ammonium oxalate solution. It was found that less trouble from cloudy filtrates was experienced if this as well as the barium sulfate precipitate spoken of in the next paragraph was allowed to settle for twenty-four or thirty-six hours in a warm place. It was then filtered on an ashless paper filter, ignited to the oxide in a muffle furnace, and immediately weighed.

Determination of Total Sulfur.—In the determination of total sulfur the same procedure was followed as for calcium up to the point of precipitation, when to the hot acid solution a sufficient quantity of a ten-per-cent. solution of barium chloride was added; the resulting precipitate of barium sulfate, after standing as mentioned above, was removed by means of a Gooch filter and filter pump, ignited at low redness, and weighed.

Determinations according to the above methods were made daily up to and including the tenth day, then on the thirteenth day, and again on the sixteenth day.

The results of these direct determinations are given in table I. In table II the figures given are calculated from those in table I. From the percentage of calcium thiosulfate the percentage of calcium so combined is calculated. These figures are given in the second column.

TABLE I.

DAY.	Specific gravity.	Thio-sulfate.	Calcium.	Sulfur.
1.....	1.0264	0.30%	0.72%	2.24%
2.....	1.0269	.38	.79	2.35
3.....	1.0273	.69	.83	2.33
4.....	1.0277	.87	.82	2.34
5.....	1.0281	.90	.87	2.35
6.....	1.0282	.93	.82	2.33
7.....	1.0284	.96	.83	2.35
8.....	1.0286	1.00	.85	2.36
9.....	1.0289	1.03	.85	2.35
10.....	1.0291	1.07	.84	2.35
11*				
12*				
13.....	1.0305	1.18	.84	2.35
14*				
15*				
16.....	1.0307	1.29	.86	2.36

* Not determined.

TABLE II.

DAY.	Calcium in thiosulfate.	Calcium in sulfides.	Sulfur in thiosulfate.	Sulfur in sulfides.	Per cent. calcium and sulfur of thiosulfate of total calcium and sulfur.
1.....	0.08%	0.64%	0.13%	2.11%	6.93%
2.....	.10	.69	.16	2.19	8.28
3.....	.18	.65	.29	2.04	14.87
4.....	.23	.59	.37	1.97	18.99
5.....	.24	.63	.38	1.97	19.25
6.....	.25	.57	.39	1.94	20.32
7.....	.25	.58	.40	1.95	20.44
8.....	.26	.59	.42	1.94	20.97
9.....	.27	.58	.43	1.92	21.88
10.....	.28	.56	.45	1.91	22.81
11.....					
12.....					
13.....	.31	.53	.50	1.85	25.39
14.....					
15.....					
16.....	.34	.52	.54	1.82	27.33

As previously stated, it has been assumed from the absence of appreciable quantities of sulfite and sulfate that the balance of the calcium is combined as sulfides. This figure obtained by subtracting calcium in the thiosulfate from the total calcium as given in the third column of table I.

In the third column, the sulfur calculated from the percentage of calcium thiosulfate is given, and in the fourth column the difference between this last and the total sulfur is given as sulfur in sulfides.

The percentage of calcium and sulfur in calcium thiosulfate to the total calcium and sulfur is given in the fifth column.

The days in the first column of each table, of course, correspond.

There is much difference of opinion among authorities concerning the sulfides of calcium. Contradictory statements may be found regarding even the more common sulfide, the monosulfide, and opinions differ as to whether or not the others have ever been prepared in a pure state. According to Mendeleeff,* in an admixture with calcium thiosulfate, by boiling a solution of lime or calcium monosulfide with sulfur, calcium pentasulfide is formed, according to this reaction:



The same authority ignores the existence of any polysulfides between the mono- and the pentasulfide.

According to Dammer,† both the penta- and the tetrasulfide exist, and may be prepared by boiling calcium monosulfide with the proper proportion of sulfur and water. He recognizes two other compounds also—Herschell's crystals, having the formula, $3\text{CaO}.\text{CaS}_4.12\text{H}_2\text{O}$, and Bushner's crystals, $4\text{CaO}.\text{CaS}.18\text{H}_2\text{O}$, which may be formed under slightly modified conditions.

To quote Watts:‡ “When CaS is boiled with S and H_2O it dissolves, forming an orange-red solution, the quantity of S which goes into solution corresponds with that required to form CaS_4 and CaS_5 ; if more S is used, it is deposited on cooling the liquid; if less S than S_3 to CaS is used, some of the CaS remains undissolved. Both solutions are decomposed on concentration with precipitation of $\text{Ca}(\text{OH})_2$ and S and evolution of H_2S .”

It is seen that there are several possible compounds of calcium and sulphur which might be present in the dip. No attempts were made to separate the sulfides other than the single unsuccessful attempt by freezing, and consequently the data given in this

* Mendeleeff's Principles of Chemistry, vol. II, p. 214.

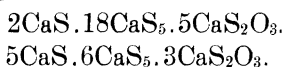
† Dr. O. Dammer, *Handbuch der Anorganischen Chemie*, II Band Theil, p. 311.

‡ Watts's Dictionary of Chemistry, vol. I, p. 214.

paper throw little light on the manner in which calcium and sulfur are combined as sulfides.

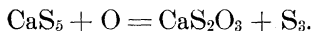
In the course of the investigation, of which this paper records but a part, many dips were analyzed. Every dip, when analyzed, gave percentages of calcium and sulfur combined as sulfides and as calcium thiosulfate. These figures varied somewhat, but could always be assigned to a solution of various mixtures of monosulfide of calcium, one or more of the polysulfides of calcium, and thiosulfate of calcium.

For the sake of simplicity and for comparison, it is assumed that the dip is a solution of a mixture of monosulfide of calcium, pentasulfide of calcium, and calcium thiosulfate, the relative proportions of which may vary, and of course would vary in a dip exposed to the air, if they decompose at different rates. Some illustrations may be given:



It is not believed that so simple a mixture is the true one, but for comparing results in the vat experiment the above possibility is given.

Some interesting facts may be noted by turning to table I. In the first vertical column it will be seen that the specific gravity is constantly and regularly increased. This increase is due, first, obviously to concentration from evaporation of the water; secondly, to the oxidation of the sulfides. In the next column it will be seen that the percentage of the calcium thiosulfate constantly increases, the greatest increase occurring in the first three days of the experiment. The total increase was 0.99 per cent. in the sixteen days, an average of 0.063 per cent. per day. This increase in calcium thiosulfate may be ascribed to two causes: First, to the concentration, as shown in the increase of specific gravity; and second, to the oxidation of polysulfides from the oxygen in the air:



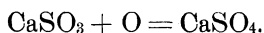
(The rate of evaporation was found in a later experiment for the same vat and same kind of dip to be 40.16 per cent. for sixteen days; so the thiosulfate from this cause alone would have increased from 0.3 per cent. on the first day to about 0.5 per cent. on the sixteenth day.)

In the third column the percentage of total calcium shows a constant and regular increase. There are at least two independent agents acting here: First, concentration acting to increase the per-

centage; and second, the decomposition of the sulfides by atmospheric carbon dioxide throwing out the calcium as calcium carbonate, and thus tending to decrease the percentage.

In the fourth column may be seen the percentages of total sulfur. After the second day this percentage remains practically constant, varying only 0.03 per cent. As with calcium, there are several changes affecting these figures: First, concentration, tending to increase the percentage; second, decomposition of sulfides by carbon dioxide in the air forming, (*a*) in the case of polysulfides, volatile hydrogen sulfide and insoluble sulfur, and, (*b*) in the case of monosulfides, volatile hydrogen sulfide only, tending to decrease the percentage; and third, oxidation to polysulfides and thiosulfates, thereby throwing sulfur out of solution. These three agencies, and perhaps others acting in the same and different directions, produce equilibrium in the percentage.

If there were sulfites or sulfates present, we would expect a further decrease in percentage total sulfur, owing to the throwing of sulfur out of solution according to the reactions,



A study of table II will reveal some other interesting facts. The columns representing calcium and sulfur calculated from the percentage of calcium thiosulfate of course show the same rate of increase as the thiosulfate column in table I.

The column giving percentages of calcium in sulfates shows a constant decrease, as would be expected, since the increase of calcium in thiosulfate must have been at the expense of the calcium in the sulfide. The same holds true for the sulfur in sulfides.

On the first day the ratio of calcium in thiosulfate to calcium in sulfides was 0.08 to 0.64, or as 1 to 8; on the sixteenth day the ratio of calcium in thiosulfate to calcium in sulfides had increased to 34 to 52, or more than 5 to 8.

Likewise the ratio on the first day of the sulfur in the thiosulfate to sulfur in the sulfides was 1 to 13, while on the sixteenth day it had increased to nearly 4 to 13. This disagreement between the two ratios would be expected if the explanation regarding the calcium and sulfur in table I be accepted. The ratio of calcium in sulfides to sulfur in sulfides on the first day is 64 to 211, while on the sixteenth day the ratio had changed to 52 to 182, or, in terms of the first, to 64 to 224. This difference in ratio in calcium and

sulfur is easily explained if it be accepted that the dip is a mixture of two or more sulfides decomposing at different rates.

Assuming, for the sake of comparison, as has been stated before, that the dip is a solution of a mixture of monosulfide, pentasulfide, and thiosulfate, then on the first day $2\text{CaS} + 7\text{CaS}_5 + \text{CaS}_2\text{O}_3$ would correspond to the different percentages, while $\text{CaS} + 9\text{CaS}_5 + 5\text{CaS}_2\text{O}_3$ would represent the mixture for the percentage given on the sixteenth day.